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Preparation of acifluorfen-based ionic liquids with fluorescent properties for enhancing biological activities and reducing the risk to the aquatic environment

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ABSTRACT: In this work, twelve novel herbicidal ionic liquids (HILs) based on acifluorfen were prepared by pairing with the fluorescent hydrazides or different alkyl chains for increasing activities and reducing negative impacts on the aquatic environment. The results showed that the fluorescence of coumarin hydrazide in the HILs was applied as the internal and supplementary light source to meet the requirement of light wavelength range of acifluorfen, which improved the phytotoxicity of acifluorfen to weeds by enhancing singlet oxygen generation with increased sunlight utilization. The herbicidal activities of HILs were related positively with the length of chain of cation under high light intensity and depended mainly on fluorescence characteristic of cation under low light intensity. And the double salt IL forms of acifluorfen containing coumarin hydrazide and n-hexadecyltrimethylammonium had enhanced efficacies against broadleaf weeds in the field. Compared with acifluorfen sodium, HILs had lower water solubility, better surface activity, weaker mobility in soils, and higher decomposition temperature. These results demonstrated that HILs containing different cations provided a wider scope for fine-tuning of the physicochemical and biological properties of herbicides and established a promising way for the development of environmentally friendly herbicidal formulations.

KEYWORDS: acifluorfen; ionic liquids; physicochemical properties; fluorescence; singlet oxygen; efficacy

INTRODUCTION

Ionic liquids (ILs), a kind of organic salts composed cations and anions, have more advantageous physicochemical properties such as low volatility, high ionic conductivity, unique solvation capabilities and good stability so on.[1-3] More importantly, ILs can be designed easily to meet the requirements of different applications due to the combination diversities of cations and anions.[4-6] Over the past two decades, ILs have been studied extensively in various fields and gone through development periods of first generation (ILs with desired physical properties), second generation (ILs with adjustable chemical properties) and third generation (ILs with excellent biological activities).[7,8] A flexible design of ionic liquid derivatives for herbicides can pose fascinating physicochemical properties (increased hydrophobicity and high surface activity), splendid environmental advantages (low volatility and great adsorption capacity) and excellent biological activity by choosing appropriate counterions.[9,10] Herbicidal ionic liquids (HILs) containing herbicidally active anions (e.g., 2,4-D, bentazone, bromoxynil, clopyralid, dicamba, dichlorprop, fomesafen, glyphosate, mesotrione, nicosulfuron, picloram) were prepared to optimize physicochemical properties for improving herbicide efficacies and reducing environmental risks caused by evaporation, leaching and the use of large dosage.[10-21] With the development of HILs, a more effective herbicide formulation, "double salt herbicidal ionic liquids" (DSHILs), shows more designable than single salt HILs.[22] DSHILs contain two different herbicidal anions and can't be classified as simple IL "mixtures" due to the unique synergistic effect of different ions.[23] The DSHILs can improve herbicidal efficacy, further broaden the spectrum of weed control, and reduce the risk of weed resistance.[22,24] This double salt approach is not only suitable for two herbicidal anions, it can also be used to prepare HILs by pairing one herbicidal anion with two different cations. Therefore, the development of double salt form of single herbicide is worth exploring, which may address the various shortcomings of herbicide and further expand the platform for ionic liquid applications.

According to HRAC herbicide classification system, the action mechanisms of many herbicides including triazines, bipyridyliums, diphenylethers and so on are involved in the process of photosynthesis of plants.[25] The activities of these herbicides usually required the participation of light and were directly or indirectly influenced by light intensity.[26] As a diphenyl ether herbicide, acifluorfen (ACI) (5-[2-chloro-4-(trifluoromethyl)-phenoxy]-2-nitrobenzoic acid) has been used extensively in postemergence for selectively controlling broadleaf weeds in soybeans and peanuts.[27,28] It inhibits protoporphyrinogen oxidase (PPO) and consequently induces the accumulation of protoporphyrin and other tetrapyrrole derivatives in weed cells in the presence of light.[29-33] Photo-excitation of these porphyrin derivatives in the presence of oxygen produces reactive oxygen, lipid peroxides and hydrogen peroxide in plant tissues, all of which are very harmful for cell membranes.[30,34] Therefore, the activity of ACI was highly affected by sunlight, and irradiating by weak light will lead to poor activity. However, the wavelengths of light required for ACI toxicity to weeds are between 410-615 nm, which means that ultraviolet radiation in sunlight has no impact on its herbicidal activity.[35-37] ACI is a weak acid (p*K*a = 3.50) and usually marketed in the form of sodium salt.[38,39] It has strong leachability (leaching potential index = 3.15) because the water solubilities of ACI acid and sodium salt are 120 mg L^{-1} and 250, 000 mg L^{-1} respectively.[40,41] This herbicide is also stable to hydrolysis and difficultly photodegraded, and thus increases the possibility of ground and surface water contamination.[42] In addition, ACI exhibits a certain extent toxicity to aquatic organisms with LC_{50} values from 17 mg L^{-1} to 61 mg L^{-1}.[43] Therefore, it is an urgent task to construct a novel form of ACI to improve efficacies by increasing sunlight utilization and reduce negative impacts on the aquatic environment.

ILs could exhibit robust fluorescence properties by introduction of fluorescent groups and afford a broad application prospect in solar cells and organic light-emitting diodes.[44-47] In this study, novel HILs based on ACI were prepared by paired with cations derived from natural occurring substances with good fluorescence properties, such as salicylic acid and coumarin, to increase efficacies by improving the sunlight utilization and reduce the negative impacts on the aquatic environment by optimizing physicochemical properties. The thermal stability, fluorescence spectrum, singlet oxygen, water solubility, surface activity, leaching and herbicidal activity (greenhouse and field) of prepared HILs were determined and investigated.

MATERIALS AND METHODS

Materials. Acifluorfen (99% purity) was purchased from Qingdao Hansen Biologic Science Co., Ltd. Methanol, ethanol, dichloromethane, *N, N*-dimethylformamide (DMF), sulfuric acid, phosphoric acid, sodium carbonate, potassium hydroxide, hydrazine hydrate (80%), tetramethylammonium (Tma) chloride, tetrabutylammonium (Tba) bromide, dodecyltrimethylammonium (Tda) bromide and n-hexadecyltrimethylammonium (Cet) chloride were analytical grade reagent and purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Salicylic acid, 3-hydroxy-2-naphthoic acid, 1,3-diphenylisobenzofuran (DPBF), protoporphyrin IX, and coumarin-3-carboxylic acid were analytical grade and purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Acetonitrile was high performance liquid chromatography (HPLC) grade and supplied from J.T. Baker (Phillipsburg, NJ, USA). The ultrapure water was obtained by using a Millipore water purification system (Millipore, Billerica, MA, USA).

Apparatus.^{1}H and ^{13}C NMR data were tested on a Bruker Avance DPX 300 MHz NMR spectrometer (Bruker, Germany) at 25 ℃. The NETZSCH STA 449F5 (Germany) was used to conduct the thermogravimetric analysis (TGA). Melting point values were recorded by a SGWX-4B microscopic melting point apparatus (SPSIC, China). Surface tension was determined by a JK 99B analyzer (Powereach, China, resolution < 0.05 mN m^{-1}). Fluorescence spectrometer (FluoroMax®-4) was applied for the determination of scanned excitation and emission spectra of the sample. LI-6400 portable photosynthesis system (Li-Cor Inc., USA) was used to detect light intensity. Chlorophyll meter SPAD-502 Plus (Konica Minolta Inc., Japan) was used to measure chlorophyll content. A HPLC system, consisting of two LC-20ATvp pumps and an SPD-20Avp ultraviolet detector (Shimadzu, Japan), was used for analysis. A reversed phase kromasil ODS C18 column (250 mm × 4.6 mm, 5 μm) was applied for separation at room temperature. The mobile phases were acetonitrile (eluent A) and water with phosphoric acid (pH = 2.8, eluent B) (70/30, v/v). Injection volume was 20 μL, and the detection wavelength was 290 nm. The flow rate was constant at 1.0 mL min^{-1}, and the column was kept at normal temperature.

Preparation of HILs. Synthesis of carboxylic esters (Est1-3). Sulfuric acid (1 mmol) was dissolved in organic solvent (methanol or ethanol) (30 mL) at ambient temperature, and then the corresponding carboxylic acid (compounds 1-3) (10 mmol) added. The mixture was heated and stirred under reflux for 10 h. Reaction was monitored by thin layer chromatography (TLC). After reaction being finished, the solvent was evaporated under vacuum and the residue was washed three times with saturated solutions of sodium carbonate. Then, the aqueous solution was extracted with dichloromethane. Finally, the desired compound was obtained after the removal of dichloromethane and used in the next reaction.

Synthesis of carboxylic acid hydrazides (Frc1-3) from Est1-3. Frc1-2: ester (Est1 or Est2) (3 mmol) and hydrazine hydrate (9 mmol) were solubilized in ethanol (30 mL). The mixture was heated and stirred under reflux for 12 h. Reaction was monitored by TLC. After reaction being finished, the solvent was evaporated and crude product was recrystallized in ethanol to obtain the desired hydrazide.

Frc3: ethyl-3-coumarincarboxylate (Est3) (2 mmol) was added into a round-bottom flask containing hydrazine hydrate (2 mmol) and 30 mL of ethanol as the solvent. The mixture was stirred for 24 h at 25 ℃. The reaction was monitored by TLC. After reaction being finished, the crude product was recrystallized in the solvent to obtain Frc3.

Synthesis of HIL1-12. The preparation method was performed following the previously reported procedure.[48,24] HIL1-3: ACI (10 mmol), hydrazides (10 mmol), and methanol were mixed in a round-bottom flask. The mixture was heated and stirred under reflux for 3 h. After reaction finished, HILs were obtained via the removal of methanol. HIL4-7: quaternary ammonium chloride or bromide (3 mmol) was dissolved in anhydrous methanol (20 mL) in a round-bottom flask. Next, potassium hydroxide (3 mmol) dissolved in anhydrous methanol (10 mL) was added. The mixture was stirred for 2 h at 25 ℃. After the filtration of the potassium chloride or bromide, ACI (3 mmol) was introduced into the methanolic solution of quaternary ammonium hydroxide. The reaction was stirred for another 1 h at 25 ºC. HILs (4-7) were obtained via the removal of the solvents. $[ACI][Frc3]_{1-m}[Cet]_m$: HILs(8-12) were studied for m =0.1, 0.3, 0.5, 0.7, and 0.9 respectively. ACI (5 mmol) was dissolved in methanol in a round-bottom flask. Next, the same stoichiometric amount (5 mmol) of a mixture of Frc3 and Cet hydroxide was added and the reaction was heated and stirred under reflux for 3 h. Then, after the removal of the solvents, the desired HIL8-12 were obtained.

Thermal analysis of HILs. The studies of thermal stability of HILs were performed using TGA. The analysis consisted of sampling a mass of 3-15 mg, which was heated from room temperature to 500 ℃ at a constant rate of 10 ℃ min^{-1} with nitrogen as an insert gas. The mass of every sample was as follows: 8.79 mg (HIL1); 4.72 mg (HIL2); 6.10 mg (HIL3); 5.00 mg (HIL4); 7.11 mg (HIL5); 11.47 (HIL6); 6.08 mg (HIL7); 5.63 mg (HIL12).

Procedure of fluorescence measurement of HILs. HIL1-3 were diluted in methanol to obtain a final concentration of 20 mg L^{-1}. Fluorescence excitation and emission spectra were recorded using FluoroMax®-4 with a 10 × 10 mm quartz cuvette at room temperature. The excitation and emission wavelengths were set respectively in the range of 200-400 nm and 400-600 nm. The excitation and emission slit widths were both set to 5 nm. Moreover, the fluorescence emission intensities of AS, HIL3, HIL7-12 were also evaluated by observing the fluorescence color at the concentration of 300 mg L^{-1} of ACI in a mixture of methanol and water (> 99% of total volume) under 366 nm UV light.

Detection of singlet oxygen. The singlet oxygen generation of HIL3 was explored by testing the degradation of DPBF (a singlet oxygen quencher with maximum absorption wavelength at 411 nm).[49] In a typical experiment, a 1 mL of DMF solution containing HIL3 (1 μM), protoporphyrin IX (1 μM), and DPBF (100 μM) was put into a 1 cm quartz cell in the dark. Then, the ultraviolet lamp (Emax=366 nm) was applied as the irradiation source. After 10 minutes of irradiation, the absorption spectra of the solution were recorded by a UV-Vis spectrophotometer.

Water solubility. The water solubilities of HILs at different pH (pH = 5, 7, and 9) at constant temperature were evaluated in phosphate buffer solutions (PBS) with the classic saturation shake-flask method.[50] In brief, HILs were weighed into the tubes (each tube with 10 mL PBS) until the emergence of surplus undissolved HILs. Then, these tubes were shaking on a shaker for 48 h. At the end of shaking, the suspensions in the tubes were centrifuged at 8000 rpm for 10 min. And the concentrations of filtered supernatants were determined by HPLC. Each treatment was carried out four times in the test.

Surface activity. The surface tensions of the synthetized HILs were determined with the Wilhelmy plate method at room temperature.[51] Before the test, a series of aqueous solutions of HILs with different concentrations were prepared using ultrapure water and the instrument needed to be calibrated with ultrapure water. The sensing platinum plate rinsed and dried was placed perpendicular and then immersed slowly into the prepared liquid sample until the formation of equilibrium between surface tension of the sample and other related forces. The value of surface tension of the synthetized compound was recorded by a tensiometer balance sensor. The value of critical micelle concentration (CMC) was determined from the intersection of two straight lines of surface tension γ versus logarithm bulk concentration (log C) of compound. Each treatment was carried out four times in the test.

Leaching test. The mobilities of HILs in the natural soils were evaluated through soil thin layer chromatograph (soil TLC).[52] The preparation of soil TLC plates, treatment conditions of test samples, and definition of R_f values were similar to our previous researches.[10,15] Firstly, the fine air-dried soil particles were obtained through a 250-μm meshed sieve. Soil TLC plates with 0.5 mm thickness were prepared by spreading the air-dried soil/water (4/3, m/m) slurry onto grass plates (20 × 20 cm) with the use of a TLC spreader. Two horizontal lines at distance of 1.5 cm and 11.5 cm were scribed on each plate above the base when the plates had been air-dried at ambient temperature for 24 h. Then the test compound (3 μg) dissolved in methanol was spotted on the bottom edge of the plate with a microsyringe at 1.5 cm. After 3 hours, the plates were put into a closed chromatographic tank with ultrapure water at a height of 0.5 cm with angle of inclination of 30º. When the water reached the 11.5 cm line, the plates were taken out and dried at ambient temperature. R_f values were calculated according to the furthest distance traveled by the test HILs divided by the distance traveled by the eluent front.

Greenhouse experiment. The herbicidal activity tests were done in the experimental greenhouse of China Agricultural University (the Haidian district, Beijing) in June 2018. Common amaranth (*Amaranthus retroflexus*) was chosen to evaluate the herbicidal efficacy of HILs. *Amaranthus retroflexus* were grown in square plastic pots with the size of 7 (length) × 7 (width) × 8 (height) cm containing nutrition soil and vermiculite (v/v 3:1). The nutrition soil texture is loam with pH=7.14 and 5% of organic carbon content. The greenhouse temperature in daytime was 26 ± 2 ℃, and the night temperature was 15 ± 2 ℃. Average day/night hours were 14/10 in the plant growth stages. Water was used for the irrigation of the plants. Ten days after emergence, the plants were thinned and about four seedlings that grow at the same rate were left in per pot. ACI-sodium (AS) and HILs dissolved in a mixture of methanol and water (> 99% of total volume) were applied using a microaerosol sprayer when the plants were at four–six leaf stage (about 15 days). Each pot was treated with 2.5 mL of drug solution and water was used as the blank controls. The test plants were divided into three groups (group A, group B and group C). Group A was sprayed with drug solutions of AS and HIL1-7 at doses of 50, 150, and 300 mg L^{-1}. Group B and group C were sprayed with drug solutions of HIL3, HIL7-12 at dose of 300 mg L^{-1}, respectively. Then, group A and group B were placed in the sunlight (PAR_{max} = 820 µmol m^{-2} s^{-1}) as high light intensity treatment and group C was placed in the weak light (PAR_{max} = 140 µmol m^{-2} s^{-1}) as low light intensity by the use of two layers of shade nets. Each treatment was carried out four times. At different days after treatment (DAT), the fresh weights and the leaf SPAD values in aboveground parts of plant under different treatments were determined and recorded. In this experiment, herbicidal activities were evaluated by fresh weight reduction (FWR) and chlorophyll content reduction (CCR) of test plants. The FWR and CCR were calculated as follows: $(W_1 – W_2)/W_1 \times 100\%$, where W_1 and W_2 represent control groups and treatment groups, respectively.

Field experiments. The research was conducted in no-till farmland located in Chongqing China (29°12′42″N 105°46′03″E) in April 2020. The environmental conditions in the region were average temperatures of 23/15 ℃ day/night, a humidity of about 65%, and a photoperiod of 13/11 hours day/night. Each experimental area size was designed to be identically 10 m^2 (2 m wide × 5 m long) covered with broadleaf weeds (*Conyza canadensis* (L.) Cronq. and *Gnaphalium affine* D. Don) and gramineous weeds (*Alopecurus aequalis* Sobol.). The weeds with a height of about 10 to 20 cm were in a fast growth phase. Based on the actual weed growth and the recommended doses of ACI in practical application, AS and HILs were applied at dose of 180, 270, and 360 g AI ha^{-1}. The spraying solution was prepared by dissolving the test compounds in a mixture of water and methanol (300:1 v/v). About 600 mL of solution was delivered in each area (10 m^2) using a microaerosol sprayer and a solution of water and methanol (300:1 v/v) was used as the control group. Each treatment was carried out in three replications. In this experiment, the herbicidal activity was evaluated by a visual method at 14 days after treatment (DAT). According to the standard developed by the Weed Science Society of America, the weed control efficacy was presented by using a scale of 0% (no visible damage) to 100% (complete death).

RESULTS AND DISCUSSION

Preparation of HILs. Twelve novel HILs (Table 1) were synthesized via a multi-step process for the first time. The major synthetic routes and the structures of cations are introduced in Scheme 1. The described compounds were also characterized by ^1H and ^1C NMR spectroscopy and the spectra are provided in the supplementary information. Three carboxylic acid compounds with fluorescence characteristic were esterified and then amidated with hydrazine hydrate to produce the cations containing primary amino groups. These cations were used to react with ACI to create HIL1-3. The synthesized HIL1-3 had high yields (exceeding 90%). The synthetic method of HIL1-3 may provide some new thoughts for the preparation of HILs with special function. HIL4-7 were prepared by reaction with quaternary ammonium hydroxide obtained from quaternary ammonium chloride (or bromide) using potassium hydroxide ion-exchange reaction. The counter cations were Tma, Tba, Tda and Cet, which represented quaternary ammonium with hydrocarbons of different lengths. The obtained HIL4-7 also had high yields (exceeding 95%) and their grease forms exhibited differences from the solid form of ACI.

HIL8-12 based on ACI were synthesized by merging two cations with different characteristics. ACI was reacted with a mixture of cations with the total molar amount being equal to that of ACI resulting in formation of double salt ILs. HIL8-12 with different Frc3/Cet molar rations (9:1, 7:3, 5:5, 3:7, 1:9, respectively) were obtained in high yields (94-98%) and presented the grease forms. HIL1 and HIL4-12 had melting points below 100 ℃, being classified as ACI-HILs. HIL2 and HIL3 were solids with melting points above 100 ℃, which were classified as new ACI salts. In ^1H NMR spectroscopy, the *–COOH* peak of ACI disappeared and the hydrogen protons on the benzene ring of ACI nearing the cations shifted to higher field strengths. These changes on ACI supported the ionized nature of HILs. There was no significant variation in the ^{13}C NMR spectra of these HILs.

The thermal properties of HILs. Thermal stabilities of the HILs were evaluated by TGA and the data are showed in Table 2. The melting points of all prepared HILs were less than 150 ℃ although acifluorfen has a high-melting solid (melting point being 276 ℃).[41] The decomposition temperatures of onset to 5% ($T_{onset5\%}$) and 50% (T_{onset}) sample were determined to provide accurate assessment of thermal stabilities for the synthesized compounds. On the basis of the obtained data, it can be concluded that HIL1-3 with carboxylic acid hydrazides had better thermal stabilities than HIL4-7 contained quaternary ammonium with different lengths of hydrocarbons. The data of $T_{onset5\%}$ and T_{onset} among HIL4-7 did not show a significant effect of the alkyl chain length on their thermal stabilities. The thermal properties of HIL 3 and HIL 7 showed that Frc3 had more effects on $T_{onset5\%}$ and T_{onset} than Cet, and Frc3 could improve the thermal stability of ACI. HIL 8-12 have the similar structural composition $[ACI][Frc3]_{1-m}[Cet]_m$ and HIL 12 has the biggest amount of Cet among HIL 8-12. The $T_{onset5\%}$ and T_{onset} of HIL12 were 134 ℃ and 285 ℃ respectively, which indicated that double salt forms of ACI had high thermal stability.

The fluorescence characteristics of HILs. The activities of ACI required the participation of light and were directly influenced by light intensity. However, ultraviolet radiation in sunlight isn't in the scope of light required for ACI phytoxicity to weeds. Thus, the sunlight utilization for ACI may be increased with the help of the fluorescence characteristics of HILs. Fluorescence excitation and emission spectra of Frc1-3 and HIL1-3 recorded at different emission and excitation wavelengths accordingly are showed in Figure 1A and Figure 1B. Although Frc1-3 were synthesized by multistep reactions from carboxylic acid compounds, they still kept the fluorescence properties. The maximum excitation wavelengths (λm-ex) of Frc1-3 were 319 nm, 349 nm and 379 nm, respectively. The maximum emission wavelengths (λm-em) of Frc1-3 were 425 nm, 412 nm and 536 nm, respectively. The fluorescence intensity of Frc2 was the strongest, followed by Frc1 and Frc3 in the same experimental condition. HIL1-3 obtained by the acid-base reactions between ACI with Frc1-3 still retained the fluorescence properties. HIL1-3 exhibited the similar λm-ex and λm-em as Frc1-3 except slight reductions in the fluorescence intensity. Under 366 nm UV light, the fluorescence color of AS, HIL3, HIL7-12 are presented in Figure 1C. HIL3 showed strong yellow fluorescence, while no fluorescence was observed in AS and HIL7 at the same concentration of ACI. HIL8-12 also exhibited yellow fluorescence and their fluorescence intensities were decreased gradually with the decreasing of Frc3/Cet molar rations.

Detection of singlet oxygen. Usually, DPBF would be readily degraded to endoperoxides in the presence of singlet oxygen and the formed endoperoxides could be decomposed into the irreversible products.[53] The reaction between DPBF and singlet oxygen can easily be monitored by recording the change of the DPBF absorption at 411 nm.[54] Figure 2 illustrates the UV-Vis spectra and absorption of DPBF at 411 nm in DMF solution under the different treatments with light in 10 minutes. The results showed that DPBF treated with HIL3 and protoporphyrin IX had lower absorptions at 411 nm than DPBF treated with protoporphyrin IX under the same light, which indicated that DPBF treated with HIL3 and protoporphyrin IX produced more singlet oxygens. Therefore, it could be concluded that HIL3 enhanced the singlet oxygen generation due to the paired cation containing fluorescence characteristic.

Water solubility. The water solubilities of HIL1-12 at different pH are displayed in Table 3. The solubilities of the prepared HILs in PBS were remarkably lower than that of AS with pH ranging from 5.0 to 9.0. As an important factor to measure the environmental fate of HILs, the water solubilities of HILs could be designed by appropriate selection of counterions. Based on the solubilities of HIL4-7, the water solubilities of HILs were distinctly decreased as the increasing of alkyl chain length of cations. The obtained data on the water solubilities of HILs were also in accord with the results of previous studies.[10,13,55] The solubilities of HIL8-12 presented a declining trend with the decreasing of Frc3/Cet molar rations and were not significantly affected by pH. With the decrease of water solubilities, ionic liquids form of ACI possessing hydrophobic property could reduce the potential risks to the natural aquatic environment.

Surface activity. The values of surface tension of the synthesized HIL1-12 at room temperature are also showed in Figure 3. The surface tensions of HIL1-12 were lower than that of AS (63.42 mN m^{-1}) except HIL2. Compared with AS, the surface tensions of HIL1-5 ranging in values from 50.89 to 64.15 mN m^{-1} had no change significantly, which indicated that the cations with fluorescence groups and short alkyl chains had little influence on the surface activities. HIL6-12 showed the low surface tensions (< 32 mN m^{-1}) due to the long alkyl chains in the cations. The type of cation in the HILs played an important role in surface tension and these findings were consistent with the previous studies.[56,57] Therefore, HILs based on ACI with good surface activities were conducive for enhancing absorption of the active ingredient and thus brought a better herbicide activity.

Leaching test. The R_f values of the synthesized HIL1-12 are also shown in Figure 3. The R_f values of HILs (ranging from 0.59-0.71) indicated lower leaching possibility than that of AS (0.73). The R_f values of HIL1-7 showed that a long alkyl chain in the cation had obvious relation with the mobility capacity of HILs in soil. HIL7 possessed the lowest mobility with R_f value being 0.63 among HIL1-7. This result was also strongly associated with the water solubility. HIL8-12 pairing with two cations also exhibited low mobility with R_f values ranging from 0.59-0.65 and had more potential possibilities for interacting with organic matter in soil. The low R_f values of HILs could contribute to reducing the negative impacts of ACI on the aquatic environment.

Greenhouse experiment. The efficacies of HIL1-7 against *Amaranthus retroflexus* at the doses of 50, 150, 300 mg L^{-1} in sunlight showed that the fluorescence characteristics in ionic liquids had a positive effect on activities (Figure 4). The excellent efficacies of HILs may be derived from the improvement of the light utilization. Referring to the fluorescence characteristic of HIL3, the λm-em at 536 nm belonged to action spectrum of the activity of ACI proposed in the previous study, which was conducive to improvement of the herbicidal activity of ACI.[35] HIL7 presented a better efficacy against broadleaf weeds than AS at the concentration of 300 mg L^{-1}, and its FWR and CCR reached 86.23% and 66.68%, respectively. These results could be explained by the good lipophilicity and low surface activity of HIL7. HILs paired with Cet had the best herbicidal activity among HIL4-7, which was consistent with previous study.[22]

Based on the excellent herbicidal efficacies of HIL3 and HIL7 derived from Frc3 and Cet respectively, Frc3 and Cet were chosen as cations in the preparation of HIL8-12. The herbicidal activities of HIL3, HIL7 (without fluorescence group in cation) and HIL8-12 (with different molar rations of Frc3 and Cet) against *Amaranthus retroflexus* at the concentration of 300 mg L^{-1} under high and low light intensities respectively are shown in Figure 5. The FWR values of AS, HIL3 and HIL7 were 68.22%, 89.56% and 82.12% respectively in the sunlight, which indicated that HIL3 and HIL7 had higher herbicidal activities than AS under normal lighting conditions. In the weak light, the FWR value of HIL3 was 70.82%, while that of HIL7 was only 46.32%. These results showed the HILs with fluorescence properties had an enhanced efficacy, while low efficacy was found for HILs without fluorescence properties under low light intensity.

Compared to the single salt IL forms, double salt ILs with cations of different properties could present more excellent herbicidal activities under high and low light intensity. The FWR value of HIL11 was 94.68% in sunlight and that of HIL8 was 84.73% in the weak light. Although the cation Cet had no effect significantly on the efficacy of ACI in weak light, the fluorescence characteristics of Frc3 in the HIL8-12 could be used as the internal and supplementary light source to increase the efficacy against *Amaranthus retroflexus*. There was a certain degree of variation in the efficacies of HIL8-12. In the sunlight, HILs with low Frc3/Cet molar rations showed high efficacies with the benefit of the excellent physicochemical properties (e.g., improved lipophilicity and good surface activity). In the weak light, the utilization efficiencies of light were increased by HILs with high Frc3/Cet molar rations, and thus high efficacies were obtained. Therefore, the efficacies of HIL8-12 based on ACI could be improved by controlling Frc3/Cet molar ratio.

Field experiment. According to the results from the greenhouse experiment, HIL3, HIL7, and HIL11 were chosen as test HILs to evaluate their herbicidal activities in the field experiments. The biological activities of AS, HIL3, HIL7, and HIL11 against different weeds in no-till farmland are illustrated in Table 4. The results demonstrated that the single salt IL forms (HIL3 or HIL7) of ACI had higher herbicidal activities against broadleaf weeds than AS, especially for *Conyza canadensis* (L.) Cronq. The control efficacies of HIL3 and HIL7 on *Conyza canadensis* (L.) Cronq. were 81.3% and 83.2% respectively at the dose of 360 g AI ha^{-1} while that of AS was 75.8%. However, this improvement is not obvious in the case of nonsensitive weeds, *Alopecurus aequalis* Sobol. Hence, the impacts of different counter cations on the herbicidal activity of ACI depended on the weed species. Compared to the single salt IL forms, the double salt IL forms (HIL11) of ACI paired with Frc3 and Cet had a better herbicidal activity. In the case of *Conyza canadensis* (L.) Cronq. and *Gnaphalium affine* D. Don, HIL11 had higher efficacies about 5.4-11.5% than HIL3 and HIL7 at the dose of 360 g AI ha^{-1}. The results indicated that the double IL forms of ACI containing Frc3 and Cet had enhanced herbicidal activities in the field.

In this study, twelve novel HILs based on ACI were synthesized using fluorescence characteristic groups and alkylamines as cations. Five double salt ILs were prepared by using coumarin hydrazide and n-hexadecyltrimethylammonium as the pairing cations due to their strong fluorescence characteristic and lipophilicity, respectively. The results showed that the prepared HILs had excellent physicochemical properties, such as good thermal stability and surface activity, low water solubility, strong fluorescence characteristic, and weak mobility in soils, which could contribute to the enhancement of herbicidal activity as well as minimization of the adverse impact on aquatic environment. The phytotoxic activities against weeds in the greenhouse showed that HIL11 was the best compound under high light conditions and HIL8 would be the best one under low light conditions. Due to the presence of two different cations, the efficacies of HILs could be optimized by variation of coumarin hydrazide/n-hexadecyltrimethylammonium molar ratio. The results of field studies confirmed HILs with coumarin hydrazide and n-hexadecyltrimethylammonium as cations had the excellent herbicidal activity against broadleaf weeds. Hence, HILs containing different cations provided a wider scope for fine-tuning of the physicochemical and biological properties of herbicides.

ASSOCIATED CONTENT

Supporting Information

The ^1H and ^{13}C NMR of synthesized compounds; the CMC value and surface tension isotherms for HILs.

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Notes

The authors declare no competing financial interest.

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TABLE AND FIGURE CAPTIONS

Scheme 1. Synthetic methods of HILs and the chemical structure of cations employed in this study.

Figure 1. The scanned excitation (A) and emission (B) spectra of HIL1-3. The fluorescence of HILs under UV light of 366 nm (C).

Figure 2. A: UV-Vis spectra (A) and absorption at 411 nm (B) of DPBF in DMF solution with light at 10 minutes. (a) DPBF only, (b) DPBF with protoporphyrin IX, and (c) DPBF with HIL3 and protoporphyrin IX.

Figure 3. The interfacial surface tensions and R_f values of HILs at 25 °C.

Figure 4. The chlorophyll content reduction (A) and fresh weight reduction (B) of acifluorfen sodium (AS) and HIL1-7 under sunlight at five days after treatment. Each data point represents the mean value from at least three independent experiments. Different letters within each column indicate statistical differences at $P < 0.05$.

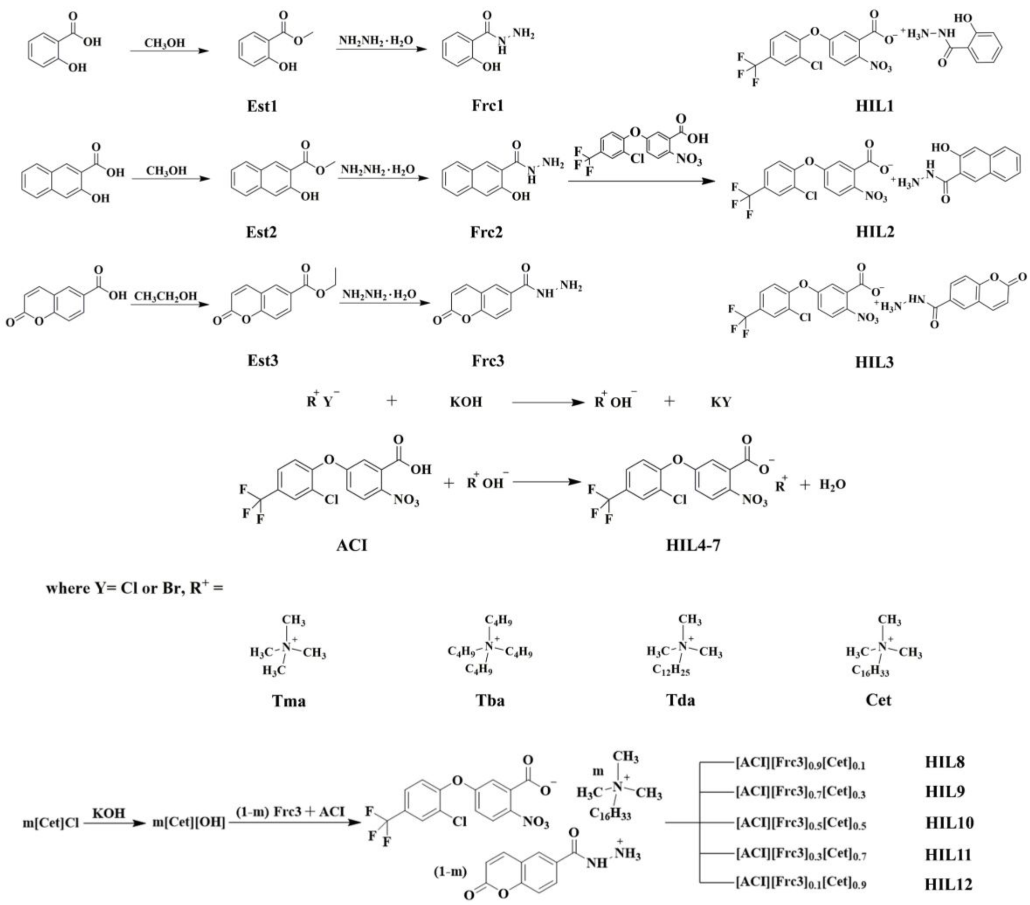
Figure 5. The fresh weight reductions of HILs at the concentration of 300 mg L^{-1} at seven days after treatment under high and weak light (upper). The pictures of *Amaranthus retroflexus* seedlings at seven days after treating with HILs at the concentration of 300 mg L^{-1} under high and weak light (under). Each data point represents the mean value from at least three independent experiments.

Table 1. Synthesized HILs based on acifluorfen. Different letters within each column indicate statistical differences at $P < 0.05$.

Table 2. The thermal properties of HILs.

Table 3. The water solubilities of HILs at different pH.

Table 4. The weed control efficacies of acifluorfen sodium (AS) and HILs at 14 days after treatment in no-till farmland.



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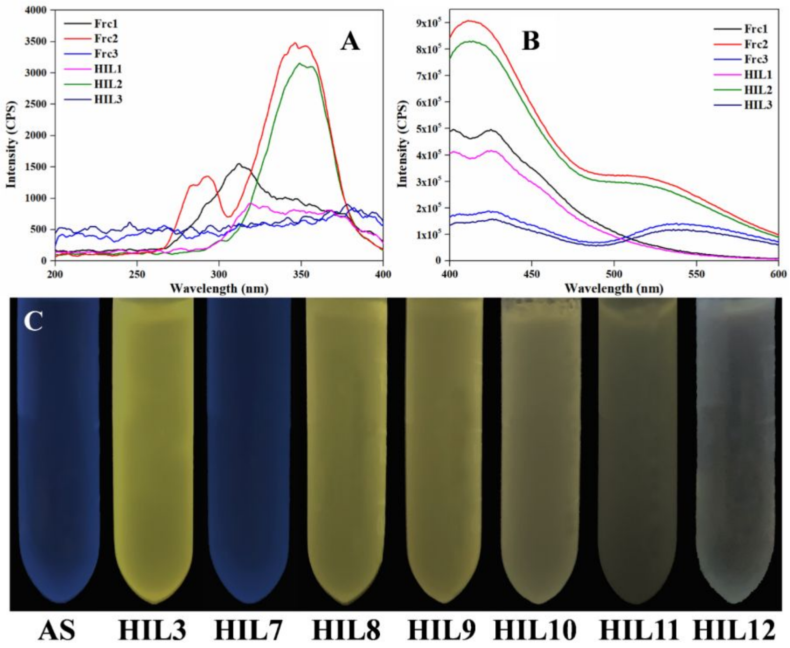

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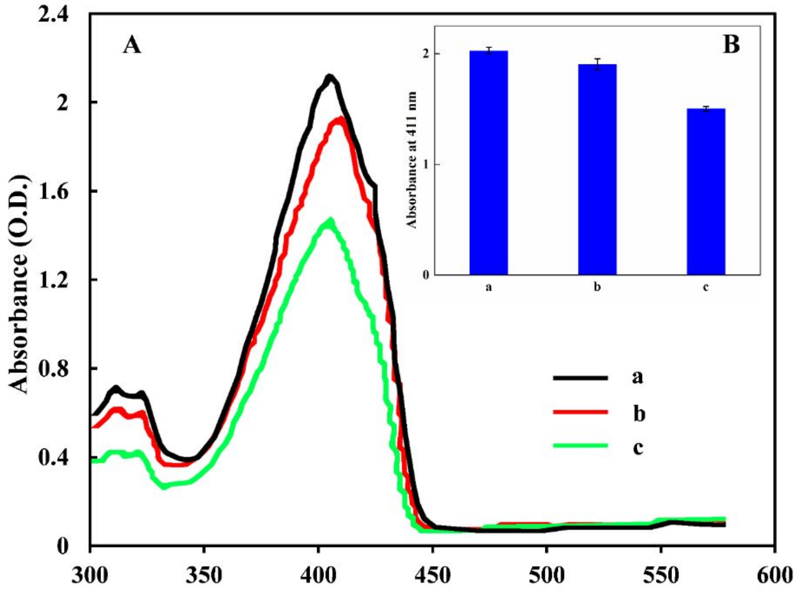

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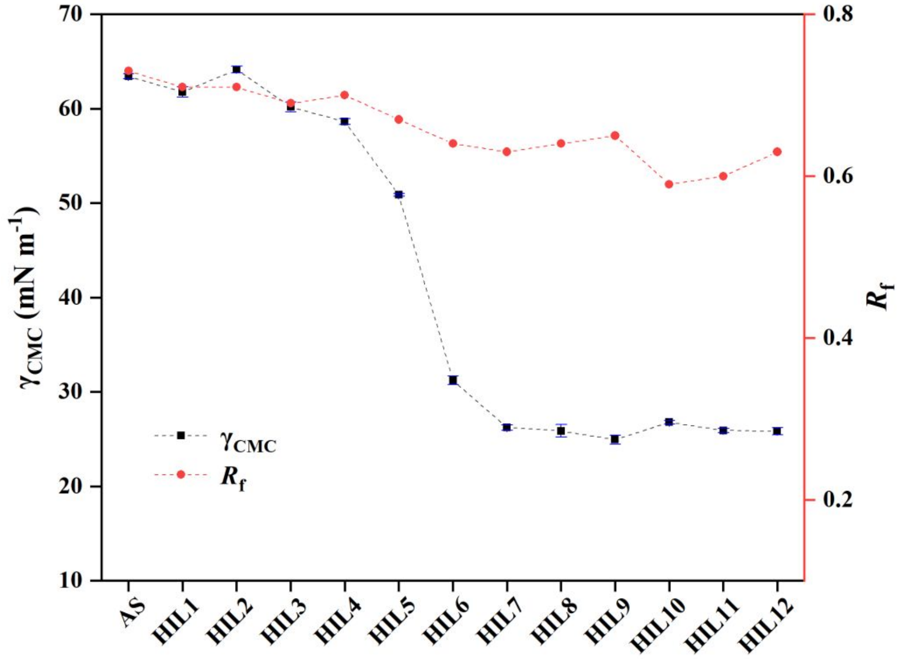

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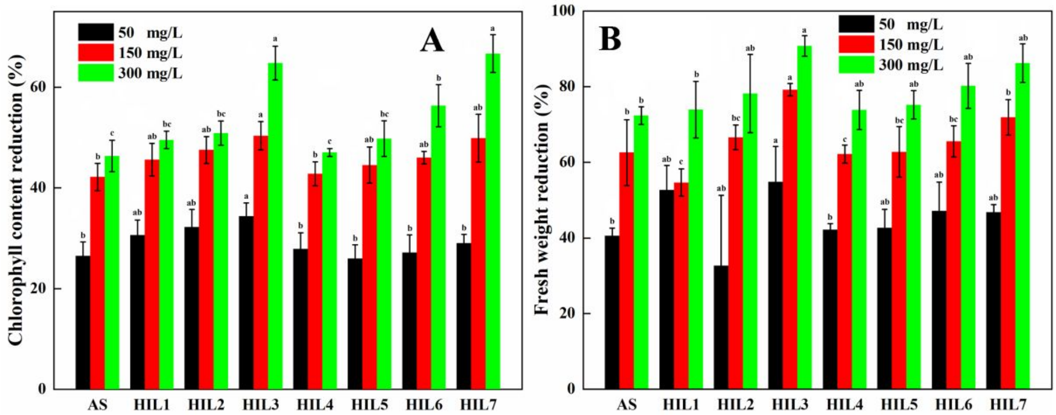

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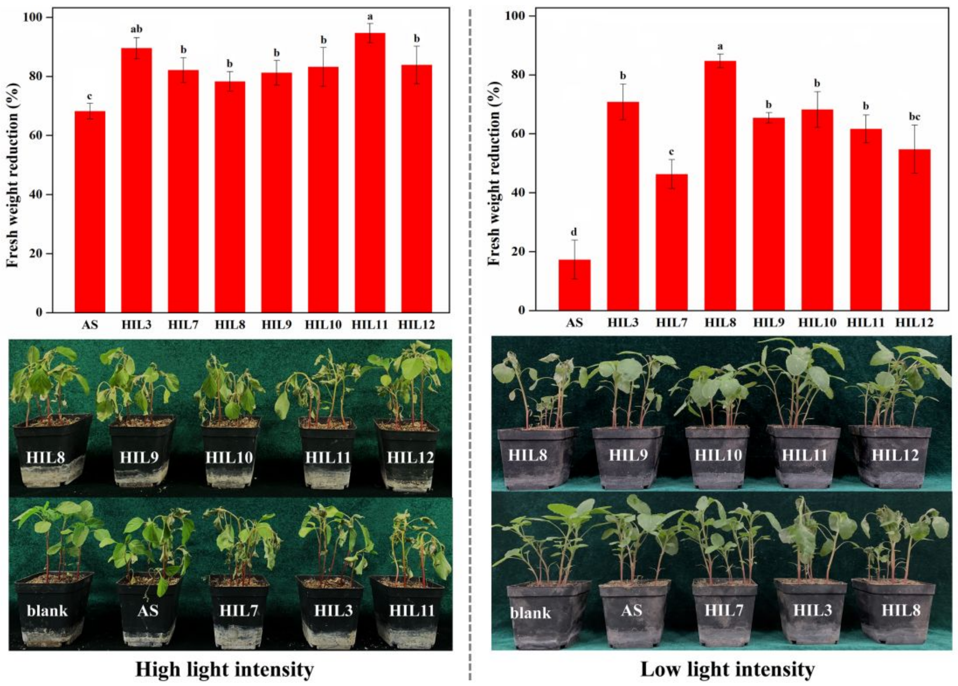

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593 Table 1. Synthesized HILs based on acifluorfen.

No.	Abbreviation	Formula $[Herb][Cat]_{m}[Cat]_{1-m}$	Color	Physical State	Yield (%)
1	HIL1	[ACI][Frc1]	brown	Solid	97
2	HIL2	[ACI][Frc2]	Yellow	Solid	95
3	HIL3	[ACI][Frc3]	Yellow	Solid	96
4	HIL4	[ACI][Tma]	Yellow	Wax	98
5	HIL5	[ACI][Tba]	Yellow	Wax	95
6	HIL6	[ACI][Tda]	Yellow	Wax	96
7	HIL7	[ACI][Cet]	Yellow	Wax	98
8	HIL8	$[ACI][Frc3]_{0.9}[Cet]_{0.1}$	Yellow	Wax	96
9	HIL9	$[ACI][Frc3]_{0.7}[Cet]_{0.3}$	Yellow	Wax	98
10	HIL10	$[ACI][Frc3]_{0.5}[Cet]_{0.5}$	Yellow	Wax	94
11	HIL11	$[ACI][Frc3]_{0.3}[Cet]_{0.7}$	Yellow	Wax	96
12	HIL12	$[ACI][Frc3]_{0.1}[Cet]_{0.9}$	Yellow	Wax	97

Table 2. The thermal properties of HILs.

No.	Abbreviation	T_m[a] (℃)	$T_{onset5\%}$[b] [℃]	T_{onset}[c] [℃]
1	HIL1	72	205	326
2	HIL2	120	204	498
3	HIL3	140	272	323
4	HIL4	–	231	279
5	HIL5	–	164	295
6	HIL6	–	169	290
7	HIL7	–	136	277
8	HIL8	–	–	–
9	HIL9	–	–	–
10	HIL10	–	–	–
11	HIL11	–	–	–
12	HIL12	–	134	285

[a] T_m, melting point. [b] $T_{onset5\%}$, decomposition temperature of 5% sample. [c] T_{onset}, decomposition temperature of 50% sample.

Table 3. The water solubilities of HILs at different pH.

No.	Abbreviation	Solubility at different pH (mg L^{-1})		
		5.0	7.0	9.0
	AS	$> 10^5$	$> 10^5$	$> 10^5$
1	HIL1	$(1.29 \pm 0.21) \times 10^3$	$(1.17 \pm 0.12) \times 10^3$	$(9.44 \pm 0.03) \times 10^2$
2	HIL2	$(2.47 \pm 0.15) \times 10^2$	$(7.11 \pm 0.28) \times 10^3$	$(3.27 \pm 0.06) \times 10^3$
3	HIL3	$(1.04 \pm 0.06) \times 10^3$	$(1.62 \pm 0.02) \times 10^3$	$(1.10 \pm 0.07) \times 10^3$
4	HIL4	$(7.85 \pm 0.22) \times 10^4$	$(1.14 \pm 0.14) \times 10^4$	$(1.06 \pm 0.11) \times 10^4$
5	HIL5	$(8.34 \pm 0.19) \times 10^2$	$(2.93 \pm 0.05) \times 10^3$	$(4.67 \pm 0.13) \times 10^3$
6	HIL6	$(9.59 \pm 0.05) \times 10^2$	$(1.02 \pm 0.16) \times 10^3$	$(1.06 \pm 0.11) \times 10^3$
7	HIL7	$(3.94 \pm 0.01) \times 10^2$	$(5.42 \pm 0.13) \times 10^2$	$(9.83 \pm 0.02) \times 10^2$
8	HIL8	$(6.58 \pm 0.11) \times 10^2$	$(7.98 \pm 0.10) \times 10^2$	$(1.09 \pm 0.15) \times 10^3$
9	HIL9	$(5.63 \pm 0.03) \times 10^2$	$(6.17 \pm 0.04) \times 10^2$	$(8.53 \pm 0.12) \times 10^2$
10	HIL10	$(3.29 \pm 0.13) \times 10^2$	$(3.84 \pm 0.01) \times 10^2$	$(4.59 \pm 0.08) \times 10^2$
11	HIL11	$(4.21 \pm 0.09) \times 10^2$	$(3.95 \pm 0.03) \times 10^2$	$(4.17 \pm 0.09) \times 10^2$
12	HIL12	$(3.83 \pm 0.08) \times 10^2$	$(4.31 \pm 0.04) \times 10^2$	$(3.78 \pm 0.05) \times 10^2$

Table 4. The weed control efficacies of acifluorfen sodium (AS) and HILs at 14 days after treatment in no-till farmland.

Salt	Control efficacy (%) with different dosage (g AI ha^{-1})								
	Conyza canadensis (L.) Cronq.			*Gnaphalium affine* D. Don			*Alopecurus aequalis* Sobol.		
	180	270	360	180	270	360	180	270	360
AS	48.3 ± 2.7 c[*]	63.1 ± 1.6 c	75.8 ± 2.3 d	35.3 ± 0.9 b	54.0 ± 2.8 c	63.2 ± 1.9 c	25.9 ± 0.9 b	38.7 ± 1.8 a	50.8 ± 0.9 a
HIL3	53.5 ± 3.3 bc	70.6 ± 2.1 b	81.3 ± 0.4 c	38.6 ± 2.8 b	55.8 ± 1.8 c	65.4 ± 1.8 c	26.3 ± 3.4 ab	43.5 ± 2.3 a	48.7 ± 2.8 a
HIL7	57.8 ± 1.9 b	69.0 ± 0.8 b	83.2 ± 1.1 b	42.9 ± 2.3 ab	60.1 ± 0.5 b	71.5 ± 2.1 b	25.1 ± 2.6 b	39.5 ± 0.9 a	50.3 ± 1.6 a
HIL11	62.9 ± 1.2 a	78.5 ± 1.7 a	90.8 ± 1.5 a	45.6 ± 1.4 a	64.7 ± 2.7 a	76.9 ± 1.8 a	28.6 ± 0.7 a	40.8 ± 3.2 a	51.2 ± 1.7 a

[*] Different letters within a column indicate statistical differences at $P < 0.05$

Table of Contents